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In re Application of: :

H. Ii et al. Art unit: 1792

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For: METHOD FOR FORMING THIN :  
FILM AND BASE AND HAVING  
THIN FILM FORMED BY SUCH :  
METHOD

## DECLARATION

Honorable Commissioner for Patents  
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Sir:

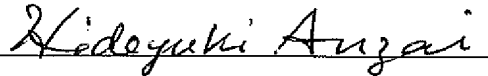
I, Hideyuki ANZAI hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 197799/2003.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with

the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

  
Hideyuki ANZAI

Dated: This 24th day of July, 2009.

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List of Documents Attached:

Title of Document:	Specifications	1
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Title of Document:	Abstract	1
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Necessity of Proof	Required
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[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

MANUFACTURING METHOD OF TRANSPARENT ELECTRICALLY CONDUCTIVE  
FILM

[SCOPE OF PATENT CLAIMS]

[Claim 1] A method for forming a transparent conductive  
film comprising a first process and a second process,

the first process comprising the step of forming a film  
on the substrate by discharging a gas 1 containing a film  
forming gas under a first discharge condition, and

the second process comprising the step of exposing the  
substrate to a gas 2 containing an oxidizing gas.

[Claim 2] The method for forming a transparent conductive  
film of claim 1, wherein the first process and the second  
process are alternately repeated a plurality of times.

[Claim 3] The method for forming a transparent conductive  
film of claim 1 or 2, wherein the second process is carried  
out in a discharge space.

[Claim 4] The method for forming a transparent conductive  
film in any one of claims 1 to 3, wherein a thickness of the  
accumulated film in the first process per batch is not more  
than 10 nm.

[Claim 5] The method for forming a transparent conductive film in any one of claims 1 to 4, wherein a temperature of the second process is 120°C or more and the oxidizing gas is oxygen.

[Claim 6] The method for forming a transparent conductive film in any one of claims 1 to 4, wherein a temperature of the second process is 80°C or more and the oxidizing gas is ozone.

[Claim 7] The method for forming a transparent conductive film in any one of claims 1 to 6, wherein in the first discharge condition, the discharge gas is nitrogen, and a high frequency electric field is applied by superposing two high frequency electric fields having different frequencies between electrodes which are facing each other.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to a manufacturing method of a transparent electrically conductive film via an atmospheric pressure plasma method.

[0002]

[PRIOR ART]

In various display elements or electrodes of thin film solar cells, employed have been transparent electrically conductive films characterized of high visible light transmittance and low resistance.

[0003]

Methods are disclosed which form a low resistant and transparent electrically conductive film by employing a DC magnetron sputter (refer, for example, to Patent Document 1). However, due to film formation in a vacuum, a batch process should be employed, resulting in problems such as low productivity and high facility cost.

[0004]

Techniques are disclosed which prepare a transparent electrically conductive film by employing an atmospheric pressure plasma method (refer, for example, to Patent Document 2). However, helium and argon, which are employed as discharge gas, are relatively expensive, whereby they are not suitable for industrial mass production. In addition, the discharge environment (either oxidative or reductive) results in difference in electric conductivity and etching properties of formed transparent electrically conductive films, whereby stable performance has not been realized.

[0005]

Further, the use of less expensive gas such as oxygen gas, nitrogen gas, or carbon dioxide in air components, as discharge gas other than rare gas, require in high voltage for discharge initiation and in a high frequency electric field, stable discharge has not been realized, whereby it has been difficult to form a stable thin film.

[0006]

Therefore, disclosure is made in which by employing a pulse electric field as an electric field, it is possible to achieve discharge of gas such as nitrogen gas exhibiting high discharge initiation voltage (refer, for example, to Patent Document 3). However, plasma density has been low and the desired quality film has not been obtained. In addition, the film forming rate has been low and the productivity has been much lower than desired.

[0007]

The present applicants discovered a method in which by employing an interval between counter electrodes and by applying two types of superimposed high frequency voltages, it was possible to generate high density plasma even for discharge gas, such as nitrogen, which exhibited high discharge initiation voltage and enable a high rate of film



formation and further at low cost and safety, as well as a decrease in environmental load.

[0008]

Based on the aforesaid method, a stable thin film forming method at a high film forming rate was achievable by employing less expensive nitrogen gas as discharge gas. However, it was found that when employed for formation of a transparent electrically conductive film employing metal doped metal oxides, a thin film of a high electric resistance and a low etching rate resulted.

[0009]

(Patent Document 1)

Japanese Patent Publication Open to Public Inspection  
(hereinafter referred to as JP-A) No. 6-318406

[0010]

(Patent Document 2)

JP-A No. 2000-303175

[0011]

(Patent Document 3)

JP-A No. 10-154598

[0012]

[PROBLEMS TO BE SOLVED BY THIS INVENTION]

In view of the foregoing, the present invention was achieved. An object of the present invention is to provide a manufacturing method of a stable transparent electrically conductive film of excellent transparency, high electric conductivity (a low resistivity value), and excellent etching properties, by employing an atmospheric pressure plasma method, and further to a manufacturing method of a stable transparent electrically conductive film by employing less expensive and safer discharge gas such as nitrogen gas.

[0013]

[MEANS TO SOLVE THE PROBLEMS]

The inventors of the present invention made diligent investigations, and it was possible to overcome the aforesaid problems via the embodiments of the present invention.

[0014]

Namely, in a manufacturing method of a transparent electrically conductive film, it was discovered that it was possible to manufacture a transparent electrically conductive film of excellent transparency, high electric conductivity, and excellent etching properties in such a manner that during a first process, a thin film was formed via the atmospheric pressure plasma method and in a secondary process, processing was carried out under an oxidative condition.

[0015]

(1) In a manufacturing method of a transparent electrically conductive film, a manufacturing method of a transparent electrically conductive film wherein at least a first process and a second process are provided, and during the first process, a film is accumulated on a substrate under the first gas condition incorporating film forming gas and the first discharge condition, and during the second process, the aforesaid substrate is exposed under the second gas condition incorporating at least oxidative gas.

[0016]

(2) The manufacturing method of a transparent electrically conductive film, described in (1), wherein the aforesaid first process and the aforesaid second process are alternately repeated a plurality of times.

[0017]

(3) The manufacturing method of a transparent electrically conductive film, described in (1) or (2), wherein the aforesaid second process is carried out in a discharge space.

[0018]

(4) The manufacturing method of a transparent electrically conductive film, described in any one of (1) - (3), wherein

in the aforesaid first process, the thickness of the accumulated layer per one time is at most 10 nm.

[0019]

(5) The manufacturing method of a transparent electrically conductive film, described in any one of (1) - (4), wherein the aforesaid second process is in an environment of 120 °C or higher and the aforesaid oxidative gas is oxygen gas.

[0020]

(6) The manufacturing method of a transparent electrically conductive film, described in any one of (1) - (4), wherein the aforesaid second process is in an environment of 80 °C or higher and the aforesaid oxidative gas is ozone gas.

[0021]

(7) The manufacturing method of a transparent electrically conductive film, described in any one of (1) - (6), wherein under the aforesaid first discharge condition, nitrogen gas is employed as a discharge gas and two types of high frequency voltages which differ in frequency are superimposed and applied between counter electrodes.

[0022]

The present invention will now be detailed.

In the atmospheric pressure plasma method employed in the present invention, a plasma discharge process is carried

out at or near atmospheric pressure, which is about 20 kPa - about 110 kPa. In order to realize the desired effects described in the present invention, a range of 93 kPa to 104 kPa is preferred.

[0023]

In the thin film forming method of the present invention, a first process (hereinafter also referred simply to as P1) and a second process (hereinafter also referred simply to as P2) are provided, and P1 is a process which forms a thin film on the substrate via the atmospheric pressure plasma method. Gases supplied between counter electrodes (being a discharge space) incorporate at least a discharge gas excited via an electric field and a thin film forming gas which forms a thin film, while converted to a plasma state or an excited state via receiving the resulting energy.

[0024]

On the other hand, P2 is a treating process in an oxidative environment which is carried out following P1 and may be carried out in an excited environment via the atmospheric pressure plasma method in the same manner as P1, or the atmospheric pressure method may not be carried out.

However, in the present invention, it is preferable to be carried out.

[0025]

As oxidative gases to form the oxidative environment, employed are oxygen gas and ozone gas. In the case of oxygen gas, the temperature is usually at least 120 °C, is preferably at least 150 °C, but is more preferably at least 170 °C, while in the case of ozone gas, the temperature usually at least 80 °C, but is preferably at least 120 °C. Though the highest temperature condition is not particularly limited, the highest temperature is preferably at most 300 °C.

[0026]

As discharge gases employed during P1, also employed may be rare gases such as helium or argon. However, by selecting discharge conditions, it is possible employ air, oxygen, nitrogen, carbon dioxide, or hydrogen. In the present invention, it is most preferable to employ nitrogen gas which is safer and less expensive, in such a manner that two types of high frequency voltages, which differ in the wavelength, are superimposed and applied between the counter electrodes.

[0027]

High frequency, as described herein, refers to one exhibiting a frequency of at least 0.5 kHz. Two types of high frequency voltages may include superimposition of sine waves, a case in which both are pulse waves, and a case in which one is a sine wave and the other is a pulse wave. Further, a third voltage component may be incorporated. Still further, it is possible to superimpose a third high frequency voltage.

[0028]

The interval between P1 and P2 processes is preferably as short as possible. It is particularly preferred that P1 and P2 processes are arranged to be adjacent to each other in the same space.

[0029]

In the atmospheric pressure plasma discharge processor which is employed in the transparent electrically conductive film forming apparatus of the present invention, discharge is carried out between the counter electrodes so that at least the discharge gas and the thin film forming gas introduced between the counter electrodes result in a plasma state, and a substrate, which stands still between the aforesaid counter electrodes or is conveyed, is exposed to gases in a plasma state, whereby a thin film is formed on the aforesaid

substrate. Further, as another system, such as a jet system, in the atmospheric plasma discharge processor, discharge is carried out between the counter electrodes which are the same as above, and gases introduced between the aforesaid counter electrodes are excited or result in a plasma state, and excited or plasma state gases are ejected in a jet state to the exterior of the aforesaid counter electrode so that the substrate near the aforesaid counter electrodes is exposed, whereby a thin film is formed on the aforesaid substrate.

[0030]

#### [DESCRIPTION OF THE INVENTION]

The transparent electrically conductive film forming apparatus, which is preferably employed in the present invention, will now be described with reference to drawings.

[0031]

FIG. 1 is a schematic constitutional view of the transparent electrically conductive film forming apparatus employed in the present invention. During first process P1 (in FIG. 1, area P1 surrounded by an alternate long and short dashed line, and which is applied to the following), counter electrodes are composed of applied electrode 1 and mobile pedestal electrode 2, and high frequency voltage is applied between the aforesaid electrodes. Discharge gas 11 and thin



film forming gas 12 are both fed through gas feeding pipe 15, pass through slit 5 formed in applied electrode 1, and flow out to a discharge space, followed by formation of gas 7 excited via the discharge plasma. By exposing the surface of substrate 4, placed on mobile pedestal electrode 2, to excited thin film forming gas 7, a thin film is formed on the substrate surface.

[0032]

Subsequently, substrate 4 is gradually conveyed to process 2 (in FIG. 1, area P2 surrounded by an alternate long and short dashed line, which is applied to the following) together with mobile pedestal electrode 2. During P2, counter electrodes are formed via applied electrode 3 and mobile pedestal electrode 2, and high frequency voltage is applied between the aforesaid electrodes. A mixed gas composed of discharge gas 13 and oxidative gas 14 is fed through feeding pipe 16 and pass through slit 6 formed in applied electrode 3, and flow out to a discharge space, followed by formation of oxidative gas 8 excited via the discharge plasma. By exposing the surface of substrate 4 placed on mobile pedestal electrode 2 to excited oxidative gas 8, the thin film on the substrate surface undergoes oxidation. Mobile pedestal electrode 2 is provided with a

moving means (not shown) which enables constant rate movement on support 9 or to stop movement.

[0033]

Further, in order to regulate the temperature of the oxidative gas, it is preferable to provide temperature regulating means 17 on feeding pipe 16.

[0034]

By carrying out reciprocation between aforesaid film forming P1 and oxidation P2 via a mobile pedestal, it is possible to form a thin film of the desired thickness.

[0035]

By applying two types of high frequency voltages, which differ in frequency, to applied electrode 1 and mobile pedestal electrode 2 which form the counter electrodes, it is possible to form preferable plasma discharge, even when employing less expensive gases such nitrogen gas. Thereafter, by quickly carrying out the process in the oxidative environment, it has become possible to form a transparent electrically conductive film, which is easily etched.

[0036]

In FIG. 2, shown is one specific example in which three types of high frequency voltages, which differ in frequency, are applied to the space between the counter electrodes.

During P1, the counter electrodes between applied electrode 1 and mobile pedestal electrode 2 are formed, and thin film forming gas feeding pipe 15 is provided, which feeds a mixed gas composed of the discharge gas and the transparent electrically conductive film forming gas. Further, it is preferable that an electrode temperature regulating means (not shown) is also provided.

[0037]

Applied electrode 1 is connected to first power source 31; first filter 33 is placed between the electrode and the power source; and mobile pedestal electrode 2 is connected to second power source 32, while second filter 34 is connected between them. First filter 33 makes it difficult to transmit an electric current at the frequency from first power source 31, and makes it easy to transmit an electric current at the frequency from second power source 32. Further, second filter 34 reversibly functions so that it makes it difficult to transmit an electric current at the frequency from second power source 32 and makes it easy to transmit an electric current at the frequency from first power source 31. Filters are employed, each of which functions as above.

[0038]

By realizing discharge conditions as above, even discharge gases, such as nitrogen gas, which result in higher discharge initiation voltage, initiate discharge and enable maintaining a high density and stable plasma state, whereby it is possible to carry out formation of a transparent electrically conductive film of high performance.

[0039]

As the frequency of the first power source, preferably employed may be at most 200 kHz. Further, this electric field waveform may be either a sine wave or a pulse. The lower limit thereof is preferably about 1 kHz.

[0040]

On the other hand, as the frequency of the second power source, preferably employed may be at least 800 kHz. As the aforesaid frequency of the second power source increases, plasma density also increases, whereby it is possible to produce a precise transparent electrically conductive film of high quality.

[0041]

It is possible to employ, during P2, the above method in which two types of high frequency voltages, which differ in frequency, is applied between the counter electrodes. In FIG. 2, P2 is provided with third power source 35 and third

filter 36 so that it is possible to separately generate the oxidative gas plasma. In the present invention, oxidation may be conducted by regulating the temperature and concentration of the oxidative gas, while no plasma is generated without employing the third power source. Further, the third power source may be omitted and applied electrodes 1 and 3 may be connected in parallel so that voltage is supplied only via the first electrode.

[0042]

FIG. 3 is a schematic constitutional view of a transparent electrically conductive film forming apparatus, having a shielding blade, which is preferably employed in the present invention. FIG. 3(a) is a top view, while FIG. 3(b) is an elevation view. During first process P1, counter electrodes are composed of applied electrodes 41, having gas passing slit 55 in the center, and mobile pedestal electrode 42. Gases fed from thin film forming gas feeding pipe 15 is ejected into a discharge space from the exit of slit 55, and result in a plasma state in the discharge space formed via the gap between the bottom surface of applied electrodes 41 and mobile pedestal electrodes 42. Substrate 4 on mobile pedestal electrode 42 is exposed to gases in a plasma state, whereby a thin film is formed. Mobile pedestal electrode 42

gradually moves while placing substrate 4 on it, whereby the thin film surface of substrate 4 is conveyed to the second process in an oxidative environment. Exposure to the oxidative gases fed from oxidative gas feeding pipe 16 is then carried out. In the present apparatus, reciprocating motion is arranged to repeat in such a manner that when movement is carried out to one end, the direction is automatically changed so that the movement is carried out to the other end. Further, it is designed so that it is possible to set the moving rate and the standing period as desired. By alternately carrying out film formation of the first process and oxidation of the second process during a specified period, it is possible to form a transparent electrically conductive film of the targeted thickness.

[0043]

In the present apparatus, in order to control the oxidative environment, it is possible to carry out heating via a heating means arranged in the oxidative gas feeding pipe and to carry out a plasma treatment by application of high frequency voltage. In the second process of the present invention, the plasma treatment may or may not be carried out, but it is preferable to carry out the plasma treatment, while it is preferable to control the heating temperature via

oxidizing gases. Further, in order to decrease effects of atmosphere, it is preferable to arrange shielding blades 10 and 11 on both sides of applied electrodes 31 and 33. The oxidative environment of the second process requires a minute amount of oxygen. Atmosphere incorporates oxygen in an excessive amount. Therefore, effects of atmosphere are lowered, and oxygen in a controlled concentration is thus fed to the substrate surface.

[0044]

As applied electrodes 1, 3, 41, and 43, as well as mobile pedestal electrodes 2 and 42, employed are those which are prepared in such a manner that after spraying ceramics as a dielectric on each of the electrically conductive base materials, sealing is carried out employing sealing materials such as inorganic compounds. The coating thickness of the ceramic dielectric on one side may be about 1 mm. As ceramic materials employed for spraying, preferably employed are alumina and silicon nitride. Of these, alumina is more preferably employed since it is more easily processed. Further, the dielectric layer may be lining processed dielectrics which are prepared by arranging inorganic materials via a glass lining.

[0045]

As electrically conductive metallic base materials, listed may be titanium metals and titanium alloys, as well as metals such as silver, platinum, stainless steel, aluminum, or iron, composite materials of ceramics and iron, and composite materials of aluminum and ceramics. Of these, titanium metals or titanium alloys are specifically preferred.

[0046]

Distance G1 (electrode gap) between the counter electrodes is determined by considering the thickness of the ceramics arranged on the electrically conductive metallic base material and the magnitude of applied voltage. The shortest distance between the dielectric surface and the surface of the electrically conductive metallic base material when dielectrics are arranged on one of the electrodes, or the distance between the dielectric surfaces when a dielectric is arranged on both above electrodes is preferably 0.1 - 20 mm, but is most preferably 0.5 - 3 mm in view of carrying out uniform discharge in both cases. Since a substrate is placed between the counter electrodes, the distance varies depending on the substrate, but the gap between the applied electrode and the substrate is preferably in the range of 0.5 - 1.5 mm.

[0047]



When employed as electrodes of various types of display elements, a patterning process which draws circuits on a substrate must be carried out and a problem whether patterning is easily carried out or not is critical for process suitability. Generally, patterning is often carried out via the photolithographic method. Since portions which need no electric conductivity are dissolved and removed via etching, the fact that the dissolving rate of the aforesaid portions in an etching liquid and no remaining residue has been a major problem. The transparent electrically conductive film prepared via the manufacturing method of the transparent electrically conductive film of the present invention exhibit excellent etching properties.

[0048]

The thickness of a thin layer of oxides or composite oxides formed as a transparent electrically conductive film is preferably in the range of 0.1 - 1,000 nm.

[0049]

Substrates which form a transparent electrically conductive film of the present invention are not particularly limited as long as it is possible to form a thin layer on the surface. Configuration and materials of the substrate are not limited as long as a uniform thin layer is formed via

exposure to mixed gas in a plasma state. In the present invention, resin films, resin sheets (plates), and glass plates are preferably employed.

[0050]

As materials of molded goods such as resin film, resin sheet, and resin molded products, listed may be cellulose esters such as cellulose triacetate, cellulose diacetate, cellulose acetate propionate, or cellulose acetate butyrate, polyesters such as polyethylene terephthalate or polyethylene naphthalate, polyolefins such as polyethylene or polypropylene, polyvinylidene chloride, polyvinyl chloride, polyvinyl alcohol, ethylene vinyl alcohol copolymer, syndiotactic polystyrene, polycarbonate, norbornene resins, polymethylpentane, polyether ketone, polyimide, polyethersulfone, polysulfone, polyether imide, polyamide, fluororesins, polymethyl acrylate, and acrylate copolymers.

[0051]

These materials may be employed individually or in appropriate combinations. Of these, preferably employed may be commercial products such as ZEONEX or ZEONOA (produced by Nippon Xeon Co., Ltd.), amorphous cyclopolyolefin resin film, ARTON (produced by Japan Synthetic Rubber Co., Ltd.), polycarbonate film, PUREACE (produced by Teijin Ltd.), or

cellulose triacetate film, KONICATAC KC4UX and KC8UX (produced by Konica Co., Ltd.). Further, even by employing materials such as polycarbonate, polyacrylate, polysulfone, or polyethersulfone, each exhibiting relatively high intrinsic birefringence, it is possible to prepare employable ones by appropriately setting liquid extruded film and melt extruded film conditions and in addition, stretching conditions in the longitudinal and transverse directions.

[0052]

Of these, as the transparent electrically conductive film of the present invention, preferably employed is a cellulose ester film which optically exhibits nearly anisotropy. The cellulose ester films include any one of cellulose triacetate film and cellulose acetate propionate, as described above. As cellulose acetate film, commercial KONICATAC KC4UX and KC8UX are useful.

[0053]

It is possible to employ those which are prepared by applying, onto the surface of these resins, gelatin, polyvinyl alcohol, acrylate resins, polyester resins, or cellulose ester resins. Further, on the thin layer side of these resin films, arranged may be an anti-glare layer, a clear hard coat layer, or a stain-resistant layer. Still

further, if desired, arranged may be an adhesive layer, an alkali barrier coat layer, a gas barrier layer, or a solvent resistant layer.

[0054]

As glass plates, listed may be soda lime glass, borosilicate glass, ultra-high purity glass, and crystal glass.

[0055]

#### [EXAMPLES]

The present invention will now be specifically described via examples, however the present invention is not limited thereby.

[0056]

#### Example 1

(Preparation of Samples 11 - 14)

By employing the transparent electrically conductive film forming apparatus shown in FIG. 1 and alkali-free glass (CORNING 7059 at a thickness of 1 mm, produced by Corning Inc.), production was carried out so that the thickness of a transparent electrically conductive film reached 100 nm via the following method.

[0057]

(Conditions during P1)

(Power Source Conditions)

Superimposing power source: low frequency side 100 kHz, 650

W/high frequency side 13.56 MHz, 450 W

Dielectric thickness: 2 mm

Electrode width: 20 mm

Applied electrode temperature: based on following Table 1

(listed as P1 electrode temperature)

Gap between electrodes: 1.5 mm

(Gas Conditions)

N<sub>2</sub> gas for vaporizing In acetyl acetonato: 10 L/minute, 170

°C

N<sub>2</sub> gas for vaporizing Sn dibutyl acetonato: 1.0 L/minute, 170

°C

Discharge gas N<sub>2</sub>: 40 L/minute

Auxiliary gas H<sub>2</sub>: 1.0 L/minute

(Conditions during P2)

(Power Source Conditions)

Dielectric thickness: 1 mm

Electrode width: 13 mm

Discharge electrode temperature: based on following Table 1

(listed as P2 electrode temperature)

Gap between electrodes: based on following Table 1, listed as  
gap between P2 electrodes

(Gas Conditions)

Discharge gas  $N_2$ : 10 L/minute

Auxiliary gas  $O_2$ : 0.01 L/minute

(Mobile pedestal Electrode)

Temperature of the mobile pedestal electrode is listed  
as lower electrode temperature in following Table 1.

[0058]

P1 and P2 were subjected to continuous reciprocating processes. Namely, applied electrode 1 of P1 and applied electrode 3 of P2 were connected in parallel and the power source on the low frequency side was connected. Mobile pedestal electrode 2 was connected to the power source on the high frequency side. It was arranged so that immediately after forming a thin film during P1, it was possible to perform oxidation of P2. In case of Sample 11, 100 nm thin film was formed via about 700 reciprocating processes over about 30 minutes.

[0059]

Table 1

	P1 Electrode Temperature (°C)	P2 Electrode Temperature (°C)	Gap between P2 Electrodes (mm)	Lower Electrode Temperature (°C)	Remarks
Sample 11	170	170	1.5	170	Present Invention
Sample 12	90	90	1.5	90	Present Invention
Sample 13	90	60	2.0	90	Present Invention
Sample 14	90	120	1.3	90	Present Invention
Sample 15	170	-	-	170	Comparative Example
Sample 16	90	-	-	90	Comparative Example
Sample 17	170	170	1.5	170	Present Invention
Sample 18	170	170	1.5	170	Present Invention

[0060]

(Preparation of Sample 15: Comparative Example)

Oxygen during P2 in preparation of Sample 11 was placed in P1 and film was formed only during P1, whereby a 100 nm thin film was formed.

[0061]

(Preparation of Sample 16: Comparative Example)

Oxygen during P2 in preparation of Sample 13 was placed during P1 and film was formed only via P1, whereby a 100 nm thin film was formed.

[0062]

(Preparation of Sample 17: Present Invention)

Under only the P1 conditions of Sample 11, 10 nm accumulation was carried out. Thereafter, the oxygen process was carried out and the above process was repeated 10 times, whereby a 100 nm thin film was formed.

[0063]

(Preparation of Sample 18: Present Invention)

Under only P1 conditions of Sample 11, 20 nm accumulation was carried out. Thereafter, the oxygen process was carried out and the above process was repeated 5 times, whereby a 100 nm thin film was formed.

[0064]

Each of the resulting samples was evaluated for the following items. Table 2 shows the evaluation results.

(Evaluation Items)

(Transmittance)

Based on JIS-R-1635, measurements were carried out by employing a spectrophotometer, type U-4000, produced by



Hitachi Ltd. The wavelength of the test light was set at 550 nm.

[0065]

<<Solid Resistivity>>

Based on JIS-R-1637, solid resistivity was determined via the four-terminal method. Measurements were carried out employing ROLESTAR GP, MCP-T600.

[0066]

<<Etching Properties>>

A photolithographic photosensitive solution was applied onto the transparent electrically conductive film of each sample, followed by drying. Subsequently, pattern exposure was carried out, and after photographic processing, immersion was carried out into the etching solution (at 30 °C) of the following composition, whereby etching was conducted.

Samples were prepared at an etching period of 30 seconds, 45 seconds, 60 seconds, 120 seconds, and 180 seconds.

Subsequently, water washing and drying were carried out. The cross-section of the boundary portion between the etched and non-etched areas of each sample after drying was observed via an electron microscope, and the state of film removal was visually evaluated.

[0067]

## &lt;Etching Solution Composition&gt;

Water, concentrated hydrochloric acid, and 40% by weight ferric chloride solution were mixed at a weight ratio of 85 : 8 : 7. The resulting mixture was employed as an etching solution.

[0068]

## &lt;Evaluation Level of Etching Patterns&gt;

- A: it was possible to remove the transparent electrically conductive film within 30 seconds, and the boundary portion of the etching pattern was excellent
- B: it was possible to remove the transparent electrically conductive film within 45 seconds, and the boundary portion of the etching pattern was excellent
- C: it was possible to remove the transparent electrically conductive film within 60 seconds, and the boundary portion of the etching pattern was excellent
- D: it was possible to remove the transparent electrically conductive film within 120 seconds, but the boundary portion of the etching pattern was not so good
- E: some of the transparent electrically conductive film remained even after 180 seconds, and the boundary portion of the etching pattern was jagged (irregular)
- F: the transparent electrically conductive film remained in

the form of islands even after 180 seconds

[0069]

Table 2

	Transmittance (%)	Volume Resistance Value ( $\times 10^{-4} \Omega \cdot \text{cm}^3$ )	Etching Properties	Remarks
Sample 11	95	2.1	A	Present Invention
Sample 12	96	2.9	B	Present Invention
Sample 13	94	1.8	A	Present Invention
Sample 14	95	2.0	A	Present Invention
Sample 15	91	40.0	F	Comparative Example
Sample 16	92	98.0	F	Comparative Example
Sample 17	94	5.8	B	Present Invention
Sample 18	94	10.0	C	Present Invention

[0070]

Based on data of Samples 15 and 16, those which were subjected to film formation via incorporation of oxygen in P1 exhibited higher solid resistivity, poor etching properties, whereby the preferred transparent electrically conductive film was not prepared. Effects result by achieving oxidation immediately after accumulation, which is described in the present invention. When the accumulation amount is increased

by prolonging P1, the resulting effects tend to decrease. It was found that the accumulation amount per one time was more preferably at most 10 nm.

[0071]

#### Example 2

(Preparation of Samples 21 - 30)

In the same manner as Example 1, preparation was carried out via the following method so that the thickness of the transparent electrically conductive film reached 100 nm.

[0072]

Incidentally, transmittance of all the resulting transparent electrically conductive films was at least 90%.

(Conditions during P1)

(Power Source Conditions)

Superimposing power source: low frequency side 100 kHz, 650

W/high frequency side 13.56 MHz, 450 W

Dielectric thickness: 2 mm

Electrode width: 20 mm

Applied electrode temperature: based on following Table 3

Gap between electrodes: 1.5 mm

(Gas Conditions)

N<sub>2</sub> gas for vaporizing In acetyl acetonato: 10 L/minute, 170

°C

N<sub>2</sub> gas for vaporizing Sn dibutyl acetonato: 1.0 L/minute, 170 °C

Discharge gas N<sub>2</sub>: 40 L/minute

Auxiliary gas H<sub>2</sub>: 1.0 L/minute

(Conditions during P2)

(Conditions A)

By employing the transparent electrically conductive film forming apparatus shown in FIG. 3, the following gases were allowed to flow to achieve oxidation.

[0073]

<Gas Conditions>

Discharge gas N<sub>2</sub>: 9 L/minute, 170 °C

Auxiliary gas O<sub>2</sub>: 1 L/minute

(Conditions B)

Discharge gas N<sub>2</sub>: 5 L/minute, 80 °C

Auxiliary gas: gas which is prepared by processing a gas mixture of N<sub>2</sub> 4.9 L/minute and O<sub>2</sub> 0.1 L/minute via an ozone generator (OR-20ZA, produced by Wako System Control Co., Ltd.)

[0074]

Table 3

	P1 Electrode Temperature (°C)	P2 Processing Condition	Oxygen Feeding Amount	Volume Resistivity ( $\times 10^{-4}$ $\Omega \cdot \text{cm}^3$ )	Etching Properties	Remarks
Sample 21	200	A	1L	1.4	A	Present Invention
Sample 22	200	A	3L	1.5	A	Present Invention
Sample 23	170	A	1L	1.6	A	Present Invention
Sample 24	90	A	1L	3.2	B	Present Invention
Sample 25	90	A	3L	4.1	C	Present Invention
Sample 26	170	B	0.1L	1.2	A	Present Invention
Sample 27	170	B	0.3L	1.7	A	Present Invention
Sample 28	90	B	0.1L	1.4	A	Present Invention
Sample 29	70	B	0.1L	2.1	B	Present Invention
Sample 30	70	B	0.3L	5.1	C	Present Invention

[0075]

In case of achieving oxidation via P1 and P2, temperature dependence resulted, and at a lower temperature, it was not possible to compensate temperature difference even though the introduced oxygen amount was increased. In the embodiment of the present invention, ozone oxidation is preferred.

[0076]

[EFFECTS OF THE INVENTION]

A first process and a second process were provided. In the first process, under a first gas condition incorporating a film forming gas and under a first discharge condition, a film is accumulated on a substrate, and subsequently, in the second process, the aforesaid substrate is exposed to a second gas condition incorporating at least an oxidative gas, whereby it was possible to provide a transparent electrically conductive film of high transparency, high electric conductivity, and excellent etching properties.

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a schematic constitutional view of the transparent electrically conductive film forming apparatus employed in the present invention.

FIG. 2 shows one specific example in which three types of high frequency voltages, which differ in frequency, are applied to the space between the counter electrodes.

FIG. 3 is a schematic constitutional view of a transparent electrically conductive film forming apparatus, having a shielding blade, which is preferably employed in the present invention.

[DESCRIPTION OF THE SYMBOLS]

1, 3, 41, and 43 applied electrodes  
2, 42 mobile pedestal electrodes  
4 substrate  
5, 6, 55, and 56 slits  
7 excited thin film forming gas  
8 excited oxidative gas  
9 supporting pedestal  
10 and 11 shielding blades  
13 discharge gas  
15 thin film forming gas feeding pipe  
16 oxidative gas feeding pipe  
17 temperature regulating means  
44 spacer  
46 and 47 applied electrode width  
P1 first process  
P2 second process  
G1 gap between electrodes  
G2 and G3 electrode slit gap



[ NAME OF THE DOCUMENT ] Drawings

FIG. 1

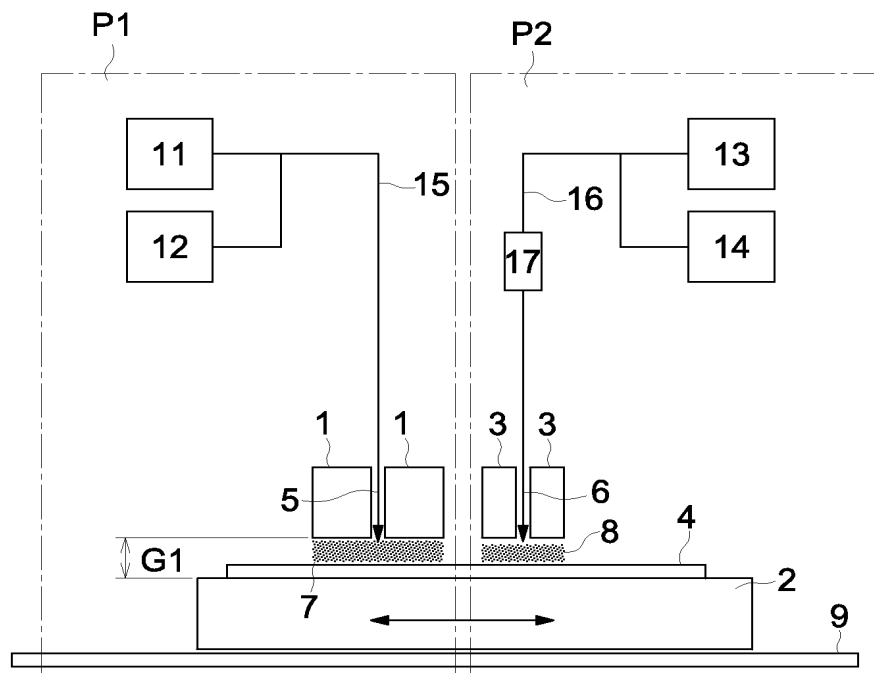


FIG. 2

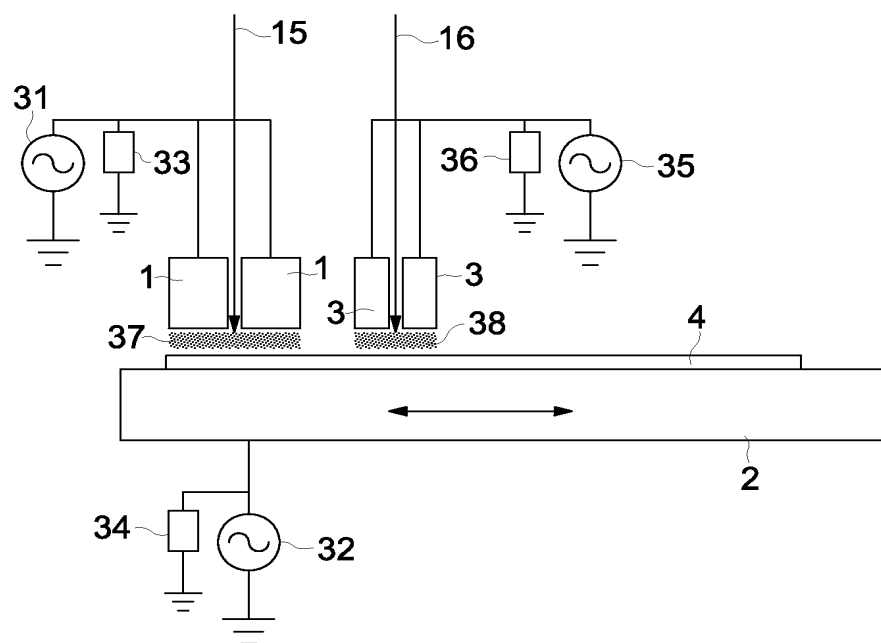
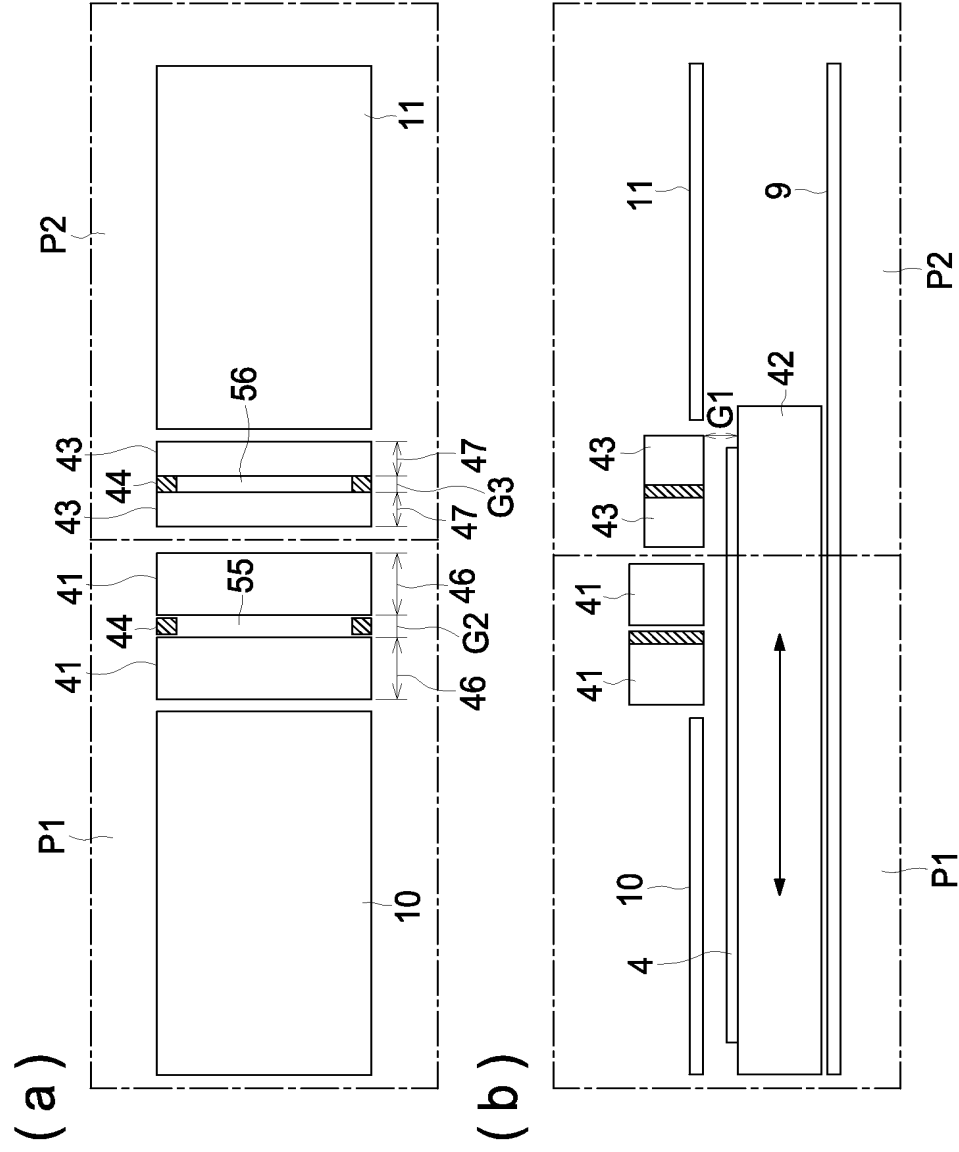


FIG. 3



[NAME OF DOCUMENT]            ABSTRACT

[SUMMARY]

[PROBLEMS TO BE SOLVED] To provide, by employing an atmospheric plasma method, a manufacturing method of a stable transparent electrically conductive film of excellent transparency, high electrical conductivity (low resistivity), and excellent etching properties, and further, to provide a manufacturing method of a stable transparent electrically conductive film by employing a less expensive and safer discharge gas, such as nitrogen.

[MEANS TO SOLVE THE PROBLEMS] In a manufacturing method of a transparent electrically conductive film, a manufacturing method of a transparent electrically conductive film wherein at least a first process and a second process are provided, and during the first process, a film is accumulated onto a substrate under the first gas conditions incorporating film forming gas and the first discharge conditions, and during the second process, the aforesaid substrate is exposed under the second gas conditions incorporating at least oxidative gas.

[SELECTED DRAWINGS] FIG. 3